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Charge-transfer induced surface conductivity for a copper based inorganic-organic hybrid

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Inorganic-organic hybrids are receiving increasing attention as they offer the opportunity to combine the robust properties of inorganic materials with the versatility of organic compounds. We have studied the electric properties of an inorganic-organic hybrid with the chemical formula: $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$. This material is a ferromagnetic insulator that can easily be processed from solution. We show that the surface conductivity of the hybrid can be increased by five orders of magnitude by covering the surface with an organic electron donor. This constitutes a novel method to dope perovskite-based materials and study their charge transport properties. © 2009 American Institute of Physics. [doi:10.1063/1.3254328]

Conventional electronics is based on inorganic materials because of their robust electric and magnetic properties. However, the usage of inorganic materials is restricted by expensive processing and fabrication processes. Organic materials are less robust, but enable inexpensive fabrication by means of spin coating and printing. Moreover, organics are flexible and their properties can be tuned by making small changes in the chemical composition. Inorganic-organic hybrid materials combine the robustness of inorganics with the processability of organics.^{1,2} For example, Kagan *et al.*³ showed that $\text{SnI}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ enables the fabrication of field effect transistors (FETs) by spin coating. The mobility approaches $1 \text{ cm}^2/\text{V s}$ but the material is unfortunately toxic and sensitive to air which makes it less suitable for applications.

We have studied the electric properties of an inorganic-organic hybrid with the chemical formula: $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$. This hybrid is air stable, non-toxic and has a similar crystal structure⁴ to the material studied by Kagan *et al.*³ The inorganic component consists of two-dimensional perovskitelike sheets that exhibit long range ferromagnetic order below 13 K.^{5,6} We have investigated the electronic transport in single crystals of this copper-based hybrid and its response to interface doping with an organic electron donor, tetrathiafulvalene (TTF). Such interfaces can display remarkable properties both in inorganic⁷ and organic materials. Recently, Alves *et al.*⁸ have demonstrated that metallicity can arise at the interface of two organic insulators. Here, we show that this method can also be used to significantly increase the conductivity in hybrid materials.

The crystals were synthesized from solution via a simple two step process. First, phenylethylamine was converted to its hydrochloride salt.⁹ Stoichiometric amounts of the organic salt and $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$ were then dissolved in water. Crystals with dimensions up to $3 \times 3 \text{ mm}^2$ and thicknesses of 0.01–1 mm, were formed by slow evaporation of the solvent.¹⁰ The structure and purity of the crystals were deter-

mined by single crystal and powder x-ray diffraction, on a Bruker APEX and D8 diffractometer, respectively.

For the electric characterization, 20 nm thick gold contacts or 100 nm thick tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) contacts were evaporated using a shadow-mask, with a gap of 90 μm between the current contacts and a gap of 30 μm between the voltage contacts. The area between the voltage contacts was 1.6 square. Platinum wires and silver paste were used to connect the contacts to the probes, preventing damage to the soft crystal. In order to dope the crystals, two methods were used. First, FETs were fabricated either by laminating the crystal onto prefabricated doped silicon with a silicon dioxide dielectric or by evaporating dielectric parylene films on top of the crystals.^{11–13} Second, a layer of electrically insulating, electron donating TTF (600 nm thick) was evaporated on top of the crystal. In this case gold contacts were used to prevent re-evaporation of the TTF-TCNQ. The temperature dependent resistance measurements were performed using a Janis cryogenic probe station sourcing a constant current (Keithley Instruments 236 electrometer), and measuring the voltage (Hewlett-Packard 3458 multimeter).

The crystal structure of the copper based inorganic-organic hybrid agrees with reports in the literature.⁴ It consists of two-dimensional sheets of corner sharing CuCl_6 octahedra (see Fig. 1). The Jahn–Teller active $\text{Cu}^{2+} d^9$ ion causes a cooperative distortion of the octahedra, which are elongated in one in-plane direction while the other in-plane and the out-of-plane Cu–Cl distances have almost the same length. This introduces an antiferrodistortive arrangement of neighboring octahedra, which is responsible for the ferromagnetic interactions. Between the inorganic copper chloride sheets, two layers of organic molecules are present. They are connected to the inorganic backbone via Coulomb interactions and hydrogen bonds. These organic molecules are not expected to contribute to the conductivity as they exhibit no π - π stacking.

Current-voltage (I-V) measurements on the undoped and doped $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ hybrid are compared in Fig. 2. All measurements were performed in the a-b plane of

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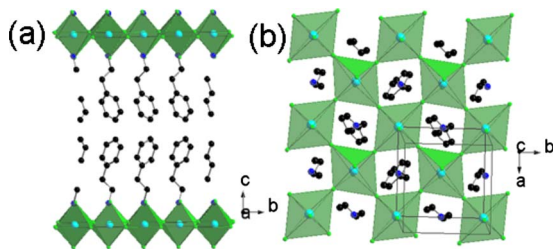


FIG. 1. (Color online) The crystal structure of $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ viewed along (a) the a -axis and (b) c -axis. The hybrid consists of perovskitelike inorganic sheets of corner sharing CuCl_6 octahedra. Adjacent sheets are 2 nm apart and separated by two layers of organic molecules. The organic molecules are connected to the inorganic part by hydrogen bonds and Coulomb interactions. The organic rings are perpendicular to each other and thus no carrier transport is expected in the organic layer.

the crystal, parallel to the inorganic sheet. Measurements using different contacts gave similar results and confirmed that the undoped $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ hybrid is a very good insulator, with a resistivity of at least $500 \text{ k}\Omega \text{ m}$ at room temperature. Attempts to increase the conductivity by making use of the field effect failed, despite the fact that the FETs were fabricated by techniques that have proven to be effective for organic crystals.^{11–13} Presently, it is unclear if this results from insufficient charge injection, trapping or contact effects.

The doped hybrid interface displays a sheet resistivity of $1 \times 10^7 \Omega/\text{sq}$, which is at least five orders of magnitude lower than the undoped hybrid. Alves *et al.*⁸ already showed that charge transfer at the interface between a TTF and a TCNQ crystal can generate up to two orders of magnitude more mobile charge carriers than in FETs. Similarly, the thin film of the electron donating insulator TTF on top of the CuCl_4 -hybrid crystal introduces charge transfer at the TTF-hybrid interface that increases the conductance by five orders of magnitude. The temperature dependence of the four-point resistivity measurements follows Arrhenius behavior (Fig. 3), from which an activation energy of approximately 0.17 eV was calculated.

Beside the gradual change in resistivity as a function of the temperature, there is a discontinuous transition near 240 K. The jump in resistivity is accompanied by a small change in activation energy from 0.16 eV below 240 K to

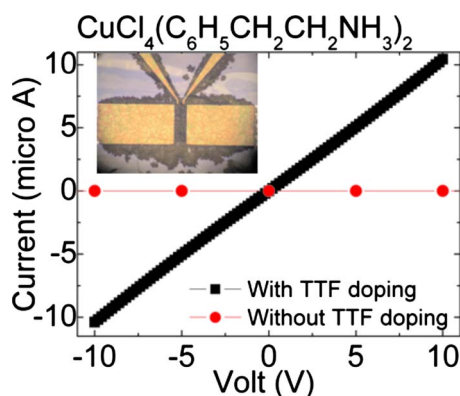


FIG. 2. (Color online) Current-voltage measurement on the Cu-hybrid crystal without (spheres) and with (squares) TTF electron doping. The conductance of the hybrid-TTF interface is five orders of magnitude larger than that of the undoped hybrid. The inset shows an image of the hybrid crystal with evaporated gold contacts and TTF on top. The TTF nucleates at the rough gold contacts and covers only part of the hybrid crystal surface.

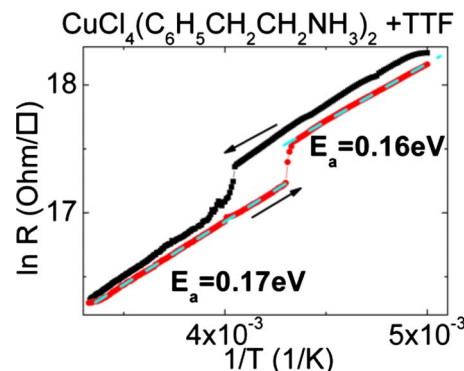


FIG. 3. (Color online) Temperature dependence of the four-point sheet resistivity of the TTF-hybrid interface. The resistivity follows Arrhenius-behavior with an activation energy of approximately 0.17 eV. The transition in the resistivity is caused by a phase transition in the hybrid.

0.17 eV above 240 K. This transition is related to a phase transition in the hybrid, which is also observed in the heat capacity and the dielectric constant of the undoped material. The origin of the transition is still under investigation and will be reported elsewhere. Nevertheless, the observation of this phase transition in the resistivity is evidence that the charge transport is associated with the hybrid-TTF interface and not restricted to the TTF-layer.

The resistivity of undoped $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ is of the order of $1 \text{ M}\Omega \text{ m}$, which is many orders of magnitudes higher than that of the structurally similar $\text{SnI}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$, which was previously studied by Kagan *et al.*³ The origin of the high resistivity in the undoped copper based hybrid is twofold. First, the Cu^{2+} and Cl^- ions are relatively small and the bonds in the inorganic layer are more ionic than in the SnI_4 -hybrid. In such an ionic bond the carriers are localized and the conductivity is low. Second, the copper ion is Jahn–Teller active, which results in an antiferrodistortive orbital ordering of the half filled $d(x^2-y^2)$ like d -orbitals.¹⁴ This orthogonal arrangement blocks the transport of charge carriers and reduces the conductivity even more. The organic molecules are not expected to contribute to the conductivity as π - π stacking is absent.

The electron-rich TTF donates electrons into the inorganic sheets at the interface of the hybrid crystal. These electrons will result in the coexistence of Cu^{2+} and Cu^+ in the perovskite layer. This mixed valence increases the conductivity. Moreover, the Cu^+ ion has a d^{10} configuration and is not Jahn–Teller active. Therefore, the doping removes the charge carrier blockade of the antiferrodistortive arrangement of the $d(z^2-x^2)$ and $d(z^2-y^2)$ type orbitals, as has been extensively studied for perovskite-based layered Cu- and Mn- oxides.¹⁵ The doping results in a higher conductivity, because it both introduces extra carriers and promotes greater delocalization. Due to the electron doping the magnetic moment at the TTF-hybrid interface is partially canceled.¹⁶ It is presently unclear how this effect influences the overall ferromagnetic state.

The carrier density at a charge-transfer interface can be estimated by comparing the measured interface sheet resistivity with the sheet resistivity of the material in the FET geometry, in which the amount of carriers can be determined.⁸ Unfortunately, the FETs of the copper hybrid did not show any gate effect. In order to obtain a rough estimate of the carrier density and the mobility, we use the

previously reported carrier density at the TTF-TCNQ interface as an upper limit, which Alves *et al.*⁸ estimated to be approximately 5×10^{14} carriers cm^{-2} . Our hybrid is a poorer electron acceptor than TCNQ, but this value of 5×10^{14} carriers cm^{-2} can, nevertheless, be used as an upper limit for the TTF-hybrid system. This doping level corresponds to one extra electron per copper atom at the TTF-hybrid interface (assuming that the carriers remain at the surface CuCl_4 layer, following the arguments of Alves *et al.*). From the number of charge carriers and the sheet resistivity of the doped TTF-hybrid interface ($1 \times 10^7 \text{ } \Omega/\text{sq}$) we calculate a lower limit for the mobility of $1 \times 10^{-3} \text{ cm}^2/\text{V s}$.

In summary, the pure hybrid $\text{CuCl}_4(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2$ is ferromagnetic insulator. The crystal interface can be doped by evaporating a layer of the electron donor TTF on top. At the doped interface the conductance is enhanced by at least five orders of magnitude and the activation energy is low, 0.17 eV. The undoped hybrid exhibits a phase transition near 240 K, which can be observed in the resistivity at the hybrid-TTF interface, providing evidence that the charge transfer is present and that the charge transport takes place at this interface.

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